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THE DIELECTRIC PROPERTIES OF SEVERAL INSULATORS

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ABSTRACT

The 300°K, 1000 Hz dielectric constant, ϵ_s , of several insulators has been measured to an accuracy of 0.01% by the method of substitution (two-fluid method). The results for different kinds of commercially available fused silica show variations of up to 1%. This spread is attributable to the presence of impurities, with water being particularly important. Several samples of naturally occurring crystalline quartz were studied, and, while values of ϵ_s for different samples of y-cut and z-cut specimens were quite uniform, the values for the x-cut samples showed a rather wide spread thus indicating the presence of impurities once again. As a first attempt at determining the level of impurities causing the variation in ϵ_s , several samples of 0.55% - 1.26% europium doped CaF_2 were measured. The results of these measurements, the first quantitative measurements of the effects of impurities on ϵ_s , are that ϵ_s is increased by about 1.5% for the various concentrations of CaF_2 : Eu studied and the effect seems to be isotropic. These results have important implications in the theory of rare earth doped alkaline earth fluorides. Also, it is found that the hydroxyl ion in NaCl has little effect on the low frequency dielectric constant at room temperature.

Finally, it is found that the dielectric constant and its temperature independent volume derivatives for MgO and Al_2O_3 are quite similar to the corresponding derivatives for the alkali halides and

the alkaline earth fluorides. These results for MgO and Al_2O_3 should be quite interesting in conjunction with future studies of their volume independent temperature derivatives.

INTRODUCTION

Accurate values of the low frequency dielectric constant are important to workers in both basic and applied research. The intrinsic theoretical interest in such a constant is rather obvious as it describes the response of a given system to an electric field. In pure materials, then, the constant gives a direct measure of the polarizability of the constituents. This polarizability is made up of four basic processes, electron-nucleus, ion-ion, molecular, and excitonic polarization. Since these relaxation processes have different frequency responses, they can be separated, and hence studied independently. In doped solids, the impurity induced dielectric relaxation mechanisms can be studied as well as the effects of the impurity on the lattice itself. This report presents the results for several pure and doped insulating materials.

The reverse of this process can be quite useful in materials testing since accurate measurement of the dielectric constant can be used to detect any dielectrically active impurity. As will be seen, the effects can be quite large although below the sensitivity of conventional measuring techniques. This process has proved quite useful in the development of a capacitive pressure gauge¹ where a high degree of uniformity in the dielectric constant of CaF_2 was correlated with a high degree of uniformity in its pressure coefficient and thus its subsequent adoption as a pressure standard.

This report presents further dielectric data from both basic and applied points of view.

SAMPLES AND PROCEDURE

Samples of various grades of fused silica were obtained from Amersil Division of Engelhard Industries, Corning Glass Works, General Electric Co., and Muffoletto Optical Co. Samples of crystalline quartz were obtained from P. R. Hoffman Co. The $\text{CaF}_2:\text{Eu}$ and $\text{NaCl}:\text{OH}$ crystals were purchased from the Harshaw Chemical Co., and Optovac, Inc., respectively and MgO and Al_2O_3 from Semi-Elements, Inc. The samples from Corning were repolished except for one schlieren grade fused silica.

The 300°K, 1000 Hz, dielectric constants of all of the samples were measured to an accuracy of 0.01% by the method of substitution² (two-fluid method)³ using the apparatus described previously by the authors.^{4,5} The pressure variation of the low frequency dielectric constants of MgO and Al_2O_3 were measured using techniques described previously by the authors.^{6,7}

RESULTS

1. Fused Silica. The most important result of these measurements is the grouping of the dielectric constants of the various grades and the difference between the grades. Nine of the twelve kinds show dielectric constants which vary in the fourth and fifth decimal place within a given grade while Homosil, Optosil 2, and Infrasil 1 vary in the third decimal place.

These results can be understood in terms of impurities. It is known that the Suprasil family is fabricated from the purest starting materials. The main difference between the W-series and the other suprasils is that

the W's are water free. Thus, the rather large difference between Suprasil 1 (2) and Suprasil W-1 (2) is due to water. The effect is probably due to the polar nature of the water since the dielectric constant increases with the water content even though the density decreases.⁸ It is also known⁹ that Infrasil and Optosil contain much less water than does Suprasil, and the present dielectric constant data agree with this trend. It would be of interest to obtain values for the amount of water in the fused silica and then correlate this with the theoretical induced dielectric constant. In addition, temperature and pressure variation of the dielectric constant and loss would yield important information on the nature of the hydroxyl relaxation mechanism.

Similar comments hold for the Optosil and Infrasil series. In each case as the "sample number" increases i.e., Optosil 1, 2, 3, the dielectric constant increases. It probably follows that the samples are progressively less pure. This is supported by the fact that the samples are correspondingly less expensive. It would be of interest to learn what selection process Amersil uses. It is of interest to note that the commercial grade samples are rather pure and uniform. This could have been fortuitous as it would be expected that these would tend to be more random.

Two samples, No. 2 Optosil 2 and No. 1 Suprasil W-2 were placed in a vacuum of about 10 milli Torr for several hours and were later remeasured. It is seen that the results before and after outgassing agree to within one part in 400,000. Thus, whatever impurities are present in these materials remain undisturbed by vacuum degassing at room temperature.

Also listed in Table I are the losses in simplex oil. As these samples were of rather uniform thickness and filled the gap almost completely, this number is a rather good measure of the loss of the sample. These losses will be measured directly in the near future. Several comments can be made. First, the loss and dielectric constant seem to be directly related within a given family. However, the loss for the highest dielectric constant materials, Suprasil W-1 and W-2 were extremely low. This is probably due to the Debye nature of the impurity and thus the variation of both the dielectric constant and loss with temperature, frequency, and pressure would be extremely interesting for these materials.

The results for Corning 7940 are listed in Table II. It is apparent from Table II that Corning 7940 is very similar to Suprasil 1 and 2. This is supported by reports of 940 ppm and 980 ppm hydroxyl concentration in Corning 7940⁸ and Suprasil⁹ respectively. It is also evident from the numbers that it probably would not be of interest to measure several samples of each grade of Corning 7940 as it appears that there are no distinct species. The different grades are probably selected especially for their optical properties. One result is of interest. That is that the sample labeled "unpolished" showed a rather large loss, significantly different from all of the others. The surface was both wavy and pitted, though the sample was optically clear. The high loss is thus probably associated with surface imperfections. It will be of interest to polish this sample and remeasure it. Also included in this batch are two Corning 7940 obtained from Muffoletto Optical Co., Baltimore, Md. The numbers for these samples fit with the rest.

The results for the General Electric Co., fused quartz are listed in Table III. These samples appear to be very similar to both Suprasil and Corning 7940. The only result of interest here is that samples measured two years ago, the "old" samples show the same trends as recently measured samples, the "new" samples. This is really more a test of the measuring process than anything else as no time variation in the dielectric constant of fused silica would be expected.

Finally, a sample of Dynasil fused quartz obtained from the Muffoletto Optical Co. was measured and the number was found to be 3.82511 as listed in Table III. This material is thus quite similar to Suprasil, Corning 7940, and General Electric fused quartz.

2. Crystalline Quartz. The results of the measurement of ϵ_s for crystalline quartz are listed in Table IV. The faces of both the x-cut and y-cut quartz are perpendicular to the C-axis, and thus the dielectric constant should be the same for these two orientations. Unfortunately, the results for the x-cut quartz are quite random. The reason is probably impurities once again. This is quite plausible as the samples were cut from naturally occurring quartz obtained from Brazil. The results for the y-cut quartz on the other hand are quite uniform and probably represent the best values of $(\epsilon_s)_\perp$ to date since the losses of the samples are rather low. The results for the z-cut quartz, $(\epsilon_s)_{11}$ were also quite uniform, however, they show a rather high loss. This is not necessarily indicative of a higher impurity content for these samples than for the y-cut samples

as it is known that the conductivity is greater along the principal axis than perpendicular to it. Higher quality samples need to be studied before an assertion can be made as to the correct values of ϵ_s for crystalline quartz. One recent worker¹⁰ reports the values to be $(\epsilon_s)_{11} = 4.60 \pm .01$ and $(\epsilon_s)_1 = 4.51 \pm .01$ at 1 kHz. Since he does not specify his source of quartz, the results are not very meaningful as the present work shows the effects of impurities to be greater than his error bars.

3. CaF_2 : Eu. As an attempt to relate the variation of the dielectric constant with impurity level, samples of CaF_2 : Eu were obtained with concentrations of 0.55%, 1%, and 1.25%. The results of the measurement of these crystals are listed in Tables V, VI, and VII respectively. The low frequency dielectric constant of undoped CaF_2 has been determined previously⁴ to be $6.7986 \pm .0003$. It should be noted that both the doped and undoped material were obtained from the same manufacturer and thus the difference in ϵ_s should be due to the Eu alone.

As seen from the tables, the dielectric constant is increased by about 1% for concentrations of Eu on the order of 1%. This implies that the Eu enters the lattice as Eu^{3+} . If the Eu were only doubly charged, it would merely replace a calcium ion and very little effect on the dielectric constant would be expected, as no new dielectric relaxation mechanisms would be introduced. When Eu enters triply charged, however, charge compensation takes place as an extra fluorine is added in the vicinity of the Eu. In this case, a new dielectric polarization process is introduced which is usually treated in terms of the fluorine hopping from site to site.

Since this process is the same in three mutually perpendicular directions, the impurity induced dielectric constant should be isotropic. This is what is observed as follows from Tables V and VII.

That the dielectric constant does not change as the concentration is increased may be due to clustering which is known from EPR measurements to occur above about 0.1%. It would be of interest to study both lower and higher concentrations as well as the pressure, temperature, and frequency variation of the impurity induced dielectric constant.

4. NaCl: OH. One system which has received a great deal of attention in recent years is NaCl: OH. This system is of particular interest because the hydroxyl ions lie along the [100] direction but are not at a lattice site. It has been observed that there is anisotropy in the electric dichroism of such a lattice and one would therefore expect anisotropy in the low frequency dielectric constant. Such an effect has been observed, in fact, at low temperatures. Very little is known about this system at higher temperatures, however. The results for the room temperature low frequency dielectric constants are listed in Table VIII. Infrared transmittance data indicates that the samples in order of increasing OH⁻ content are B, A, C in that C shows the strongest absorption at 2.8 microns and B the least.

It appears that 300°K is too high to observe anisotropy in the dielectric constant using the present methods, however a trend in the loss is seen. That is that as the hydroxyl concentration increases, the dielectric constant itself tends to increase, although the effect at room temperature

is very small. The interesting fact, however, is that the loss decreases. It would be of interest to study the variation of ϵ_s of these samples with temperature, frequency, and pressure.

5. MgO and Al_2O_3 . The pressure derivatives of capacitance for MgO and Al_2O_3 are listed in Table IX along with the isothermal compressibility and its isothermal pressure derivative. These quantities were transformed to the pressure derivatives of the static dielectric constant using the equations of Reference 6. It should be kept in mind that these equations are only approximate for Al_2O_3 in that $\chi_T/3$ is taken to be equal to the appropriate strain derivative. The resultant pressure derivatives are listed in Table X along with the low frequency dielectric constant itself. The results of other workers are also listed there. The usual poor agreement is seen as indicating the need for reliable numbers for the pressure derivatives of the dielectric constants of these materials.

Of more interest than the pressure derivatives are the volume derivatives and these were calculated using the equations of Reference 6 and the data of Table X and are listed in Table XI. It should be noted that these are exact equations for both MgO and Al_2O_3 once the pressure derivatives have been determined. The results are rather striking when compared with the corresponding values for the alkali halides⁶ and the alkaline earth fluorides.⁷ It is seen that all values are of the same order of magnitude for MgO and Al_2O_3 as for the alkali halides and the alkaline earth fluorides. This is somewhat surprising as the former are polyvalent and are not generally thought of as strongly ionic materials. It will be of interest to study the temperature and frequency variation of ϵ_s for these materials.

CONCLUSIONS

Thus, the low frequency dielectric constant can be affected quite strongly by the presence of impurities. In particular, it has been shown that 0.1% of water can increase ϵ_s for fused silica by almost 1%. This dictates a larger variation in commercially available samples than is generally thought. In addition, it has been shown that impurities in natural quartz have such an effect as to render all previous low frequency measurements not very meaningful. It will be necessary to investigate high quality cultured quartz in order to arrive at reliable values of ϵ_s for this material. Also, it has been shown that 0.55% - 1.26% of europium in CaF_2 increases the dielectric constant by about 1.5%.

On the negative side, it has been shown that the presence of hydroxyl ions in NaCl has little effect on the room temperature dielectric constant. It will be of interest to investigate ϵ_s at lower temperatures.

Finally, it has been shown that the low frequency temperature independent dielectric properties of MgO and Al_2O_3 have a great deal of similarity to those for the alkali halides. These results are rather interesting since MgO and Al_2O_3 are not usually thought of as strongly ionic materials.

It would be interesting to extend the pressure measurements to crystalline quartz, fused silica, and the doped materials. Additional information could be gained from the temperature and frequency variation of ϵ_s for all of the materials. Experiments to determine these quantities are now in progress.

TABLE I

Low Frequency Dielectric Constants and
Approximate Losses for Amersil Fused Silica

Type	ϵ_s	Loss in Simplex Oil (ppm)
Commercial		
1	3.80969	14
2	3.80931	16
3	3.80973	17
Homosil		
1	3.81087	11
2	3.81117	10
3	3.81098	10
Optosil 1		
1	3.81090	8
2	3.81079	7
3	3.81083	7
Optosil 2		
1	3.81047	15
2	3.81131 (3.81132)	13
3	3.81300	34
Optosil 3		
1	3.81127	15
2	3.81131	16
3	3.81122	16
Infrasil 1		
1	3.81156	47
2	3.81297	60
3	3.81263	58
Infrasil 2		
1	3.81322	70
2	3.81329	70
3	3.81328	70
Ultrasil		
1	3.81261	14
2	3.81254	10
3	3.81267	13

TABLE 1 (cont'd)

Type	ϵ_s	Loss in Simplex Oil (ppm)
Suprasil 1		
1	3.82990	<1
2	3.82946	<1
3	3.82975	1
Suprasil 2		
1	3.83022	1
2	3.83043	<1
3	3.83043	<1
Suprasil W-1		
1	3.80729	1
2	3.80740	1
3	3.80732	1
Suprasil W-2		
1	3.80727 (3.80726)	<1
2	3.80727	<1
3	3.80726	<1

TABLE II

Low Frequency Dielectric Constants of Corning
Code 7940 Fused Silica

Grade	ϵ_s	Loss in Simplex Oil
<u>Schlieren</u>		
Polished	3.82695	1
Unpolished	3.82758	37
Ultraviolet	3.82778	1
Optical	3.82494	3
Optical α	3.82729	10
Industrial	3.82747	2
Mirror	3.82691	8
Muffoletto 1	3.82771	
2	3.82807	

TABLE III

Low Frequency Dielectric Constants of General Electric
Fused Quartz and Dynasil Fused Silica

Sample	ϵ_s	Loss in Simplex Oil
Old		
1	3.82732	-
2	3.82876	-
3	3.82814	-
4	3.82873	-
5	3.82751	-
New		
1	3.82793	<1
2	3.82863	<1
3	3.82774	<1
4	3.82810	<1
Dynasil		
1	3.82511	<1

TABLE IV

Low Frequency Dielectric Constants of
Single Crystal Quartz

Cut	ϵ_s	Loss in Simplex Oil
X-Cut		
1	4.51784	39
2	4.52028	34
3	4.55878	47
4	4.55899	72
Y-Cut		
1	4.52099	~20
2	4.52087	~20
3	4.52086	~20
4	4.52089	~20
5	4.52096	~20
Z-Cut		
1	4.63717	~200
2	4.63719	~200
3	4.63731	~200
4	4.63719	~200
5	4.63721	~200

TABLE V

Low Frequency Dielectric Constants
of CaF_2 : Eu 0.55%

Orientation	Sample	ϵ_s	Loss in Simplex Oil
[111]	1	6.8797	341
	2	6.8795	336
[110]	1	6.8816	355
	2	6.8820	355
[100]	1	6.8782	336
	2	6.8782	347
Unknown	1	6.8756	341
	2	6.8769	344
	3	6.8754	355
	4	6.8758	340

TABLE VI

LOW FREQUENCY DIELECTRIC CONSTANTS

OF 1.00% CaF_2 : Eu

Sample	ϵ_s	Loss in Simplex Oil
1	6.8825	330
2	6.8687	290
3	6.8707	290
4	6.8682	290
5	6.8715	290

TABLE VII
 Low Frequency Dielectric Constant of
 1.26% CaF_2 : Eu

Orientation	Sample	ϵ_s	Loss in Simplex Oil
[111]	1	6.8685	296
	2	6.8715	300
[110]	1	6.8702	316
	2	6.8706	300
[100]	1	6.8795	340
	2	6.8697	291
Unknown	1	6.8678	295
	2	6.8705	308
	3	6.8694	302
	4	6.8691	290

TABLE VIII
Low Frequency Dielectric Constants of
NaCl: OH

Orientation	A	B	C
[100]	5.89527	5.89525	
	(105)	(260)	
[110]	5.89523	5.89508	
	(120)	(220)	
[111]	5.89535	5.89509	
	(140)	(260)	
Unknown	5.89517	5.89505	5.89680
	(90)	(240)	(68)
	5.89514	5.89560	5.89579
	(115)	(180)	(90)

TABLE IX

Pressure Derivatives of Capacitance and Basic Data for Transforming
These Derivatives to Pressure Derivatives of the Static
Dielectric Constant

	MgO	Al ₂ O ₃ Perpendicular to C-axis	Al ₂ O ₃ Parallel to C-axis
$\frac{1}{C_0} \left(\frac{\partial C}{\partial P} \right)_T$ (10 ⁻¹² cm ² /dy)	- 2.027	- 1.059	- 1.157
$\frac{1}{C_0} \left(\frac{\partial^2 C}{\partial P^2} \right)_T$ (10 ⁻²⁴ cm ⁴ /dy ²)	+12.7	+ 3.73	4.97
χ_T (10 ¹² cm ² /dy)	.626 (a)	.408 (b)	.408 (b)
$\left(\frac{\partial \chi_T}{\partial P} \right)_T$ (10 ⁻²⁴ cm ⁴ /dy ²)	- 1.77 (a)	- .698 (b)	- .698 (b)

References for Table IX

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TABLE X

The Low Frequency Dielectric Constants and Their
Pressure Derivatives for MgO and Al₂O₃

	MgO	Al ₂ O ₃ Perpendicular to C-axis	Al ₂ O ₃ Parallel to C-axis
ϵ_s (300°K)	9.8295	9.3986	11.5844
		9.8 (a)	12.7 (a)
$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial P} \right)_T$	- 1.818	- .923	
	- 3.2 (b)		- 1.021
(10 ⁻¹² cm ² /dy)	- 1.9 (c)	- 1.01, - 1.05 ^(a)	- 1.08, - 1.11 ^(a)
	- 1.6 (d)		
	- 1.8 (e)		
$\frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial P^2} \right)_T$	11.3	3.23	4.44
(10 ⁻²⁴ cm ⁴ /dy ²)			

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TABLE XI

Volume Derivatives of the Low Frequency Dielectric

Constants of MgO and Al_2O_3

	MgO	$\text{Al}_2\text{O}_3 \perp$	$\text{Al}_2\text{O}_3 \parallel$
$V \left(\frac{\partial \epsilon_s}{\partial V} \right)_T$	28.55	21.25	28.99
$\frac{V}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial V} \right)_T$	2.90	2.26	2.50
$V^2 \left(\frac{\partial^2 \epsilon_s}{\partial V^2} \right)_T$	126	72	158

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